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where the first A is defined in the sense of the average of an analytic functional, and the second as a multiple integral. A precisely analogous theorem holds when $f_m(x)$ instead of a broken straight line is any broken line with corners at $(0, 0)$ and at $(x_{(K)}, f(x_{(K)}))$, and consists of monotone arcs between these points. This last theorem makes our average of a functional the limit of the average of a function of a discrete set of variables, and justifies our use of the term average.

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[1] The problem of the mean of a functional has been attached by Gâteaux (*Bull. Soc. Math. de France*, 1919, pp. 47–70). The idea of using the analytic functional as a basis is there found. The actual definition, however, is essentially different, and does not lend itself readily to the treatment of the Brownian Movement, for which the present method is especially adapted.

[2] Einstein, *Leipzig, Annalen Physik*, **17**, 905.

[3] We here take $t_1, < t_2 < \ldots < t_n$.

[4] Cf. V. Volterra, *Fonctions des Lignes.*

[5] Cf. P. J. Daniell, *Annals of Mathematics*, Sept., 1919, p. 30.

ON THE CALCULATION OF THE X-RAY ABSORPTION FREQUENCIES OF THE CHEMICAL ELEMENTS

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Communicated July 23, 1921

The K critical absorption frequency of a chemical element is the highest frequency of vibration known to be characteristic of that element. In our laboratory we have measured the K critical absorption frequencies of most of the chemical elements by the ionization method. This data, together with measurements made elsewhere by the photographic method, may be found in Table 2 of a report by the author on Data Relating to X-Ray Spectra, which has been published by the National Research Council.

At a symposium on Ultra-Violet Light and X-Rays, held at the meeting of the American Association for the Advancement of Science at St. Louis in December 1919,[1] I presented a set of computations of the K critical absorption frequencies based on the Rutherford-Bohr theory of atomic structure and the mechanism of radiation. The computed values equalled the observed values to within one or two per cent. In these computations the electrons were supposed to revolve in orbits which lay in planes passing through the nucleus of the atom.

Later I presented[2] to the National Academy of Sciences and to the American Physical Society computations of these K critical absorption frequencies, calculated on the assumption that the orbits did not all lie in planes through the nucleus. I assumed that the orbits were circular, that they occurred in pairs and that the two orbits in a pair lay opposite to each other in parallel planes equi-distant from the nucleus, as represented in the figure. This gives a volume distribution of electrons. The mutual repulsion of the electrons for each other keep the orbits apart. It is necessary, however, to suppose that the electrons in the two orbits of a pair revolve in opposite directions. Otherwise they would be pulled together to form a single orbit in a plane through the nucleus (at least for elements of high atomic numbers). The revolution in opposite directions has the advantage, among others, of reducing the magnetic field due to the electrons for points at a distance from the atom to a very small value.

The theory contains three fundamental laws. The acceleration law, the angular momentum law and the frequency law. The acceleration law states that the centripetal acceleration of each electron revolving in its orbit equals the centripetal force acting on it, due to the attraction and repulsion of all the electrical charges in the atom acting according to Coulomb's inverse square law. The angular momentum law states that the angular momentum of each electron equals a whole number (called the quantum number), τ, multiplied by Planck's action constant, h, and divided by 2π. According to the frequency law, the product of h into the frequency of vibration, ν, of the radiation emitted during a shift of the electrons from one position of dynamic equilibrium to another equals the difference in the amounts of energy in the atom before and after the shift.

The first two laws cannot be true at every instant of time. One or both of them must represent average values. In the modern development of the theory a definite integral of certain generalized coördinates is equated to a multiple of h.

The theory does not determine the numbers of electrons in the various orbits. In making calculations, however, we must know how the electrons are distributed. Several authors have calculated X-ray frequencies by choosing distributions of electrons in the orbits that best fit the X-ray data themselves. I have taken a distribution suggested by the intervals between the inert gases in the sequence of chemical elements. It has long been supposed that these intervals correspond to groups of electrons in the atom that are completely filled up. From this point of view we get as the numbers of electrons in the various groups the following: the inner orbit contains two electrons. The next group consists of a pair of parallel orbits containing in all eight electrons, four in each orbit. The third group contains eight electrons, four in each of the two parallel orbits. The next group contains eighteen electrons in all, nine in each of the two parallel orbits. The fifth group also contains eighteen, nine in each orbit. The outside pair of parallel orbits contains thirty-two electrons, sixteen in each orbit. Of course, for atoms containing less than ninety-two electrons the outer groups are incomplete, or missing altogether.

To each pair of orbits belongs a certain quantum number, τ. For the inner orbit $\tau = 1$, for the second group $\tau = 2$, for the third group $\tau = 2$, for the fourth and fifth $\tau = 3$, and for the sixth group $\tau = 4$. According to this distribution the number of electrons in an orbit (except the innermost) equals the square of the orbit's quantum number.

The fundamental laws of the theory may be expressed by the following equations:

Acceleration Law........... $mv^2/a =$ Centripetal Force (1)
Angular Momentum Law.................. $mva = h/2\pi$ (2)
Frequency Law......................... $h\nu = W_1 - W_2$ (3)
Distribution Law............................ $n = \tau^2$ (4)

where m is the mass of an electron, v, its velocity, a, the radius of its orbit, and W_1 and W_2 are the total amounts of energy possessed by the atom in the two states of dynamic equilibrium.

In computing vibration frequencies we first calculate the velocity of each electron from equations 1 and 2, and then find the total energy of all the electrons, including both the potential and kinetic energies. Taking into account the change of mass of an electron with its velocity, the total energy may be represented by

$$W = \Sigma\, m_o c^2 (\sqrt{1-\beta^2} - 1),$$

where $\beta = v/c$, c being the velocity of light. If the velocity of the electron is small, as compared with the velocity of light, this expression reduces to

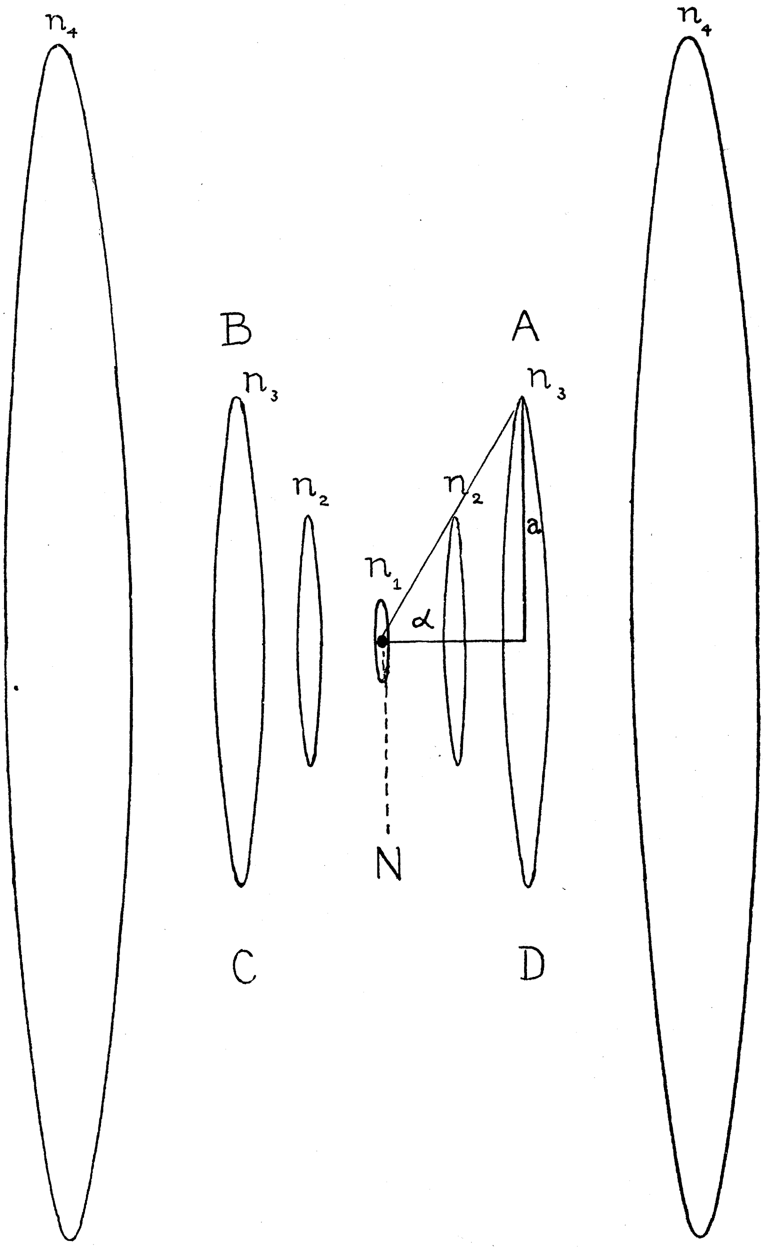
$$W = -\Sigma {}^1/_2\, m_o v^2.$$

To compute the K critical absorption frequency (according to equation 3) we must calculate the value of W for the atom, when one electron is missing from the inner orbit, and subtract from it the value of W, when this electron is in its proper place. The difference between these two terms equals h multiplied by the critical absorption frequency, ν.

Each of the terms in the expressions obtained for W contains the quantity

$$\nu_o = \frac{2\pi^2 e^4 m_o}{h^3} \qquad (5)$$

as a factor. This is the Rydberg fundamental constant. It simplifies the equations to calculate the ratio of the absorption frequency to this fundamental constant, i.e., ν/ν_o.


n_4
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n_2
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D

The terms in the expression for the frequency ratio ν/ν_0 due to the electrons in the inner orbit only are

$$2\,(N-.25)^2\,(1+{}^1/_4\,\beta^2+{}^1/_8\,\beta^4+..)-N^2(1+{}^1/_4\,\beta'^2+\beta'^4+..),\quad(6)$$

where

$$\beta=\frac{2\pi e^2(N-.25)}{ch}\qquad\beta'=\frac{2\pi e^2N}{ch}$$

and N is the atomic number of the chemical element. In this equation the relatively small forces due to electrons in orbits outside of the inner orbit have been neglected. The two series in increasing powers of β represent the correction for the change of mass of the electron with its velocity.

In calculating the velocities of the electrons in the orbits outside of the inner one, I have made several approximations. Firstly, I have assumed that the force acting on an electron, due to the electrons in orbits that are smaller than its own, is the same as it would be, if these electrons were concentrated at the nucleus of the atom. Secondly, I have neglected the part of the force acting on an electron, due to the electrons in orbits that are larger than its own. Thirdly, the calculation of the force acting on an electron in an orbit, say at A in the figure, due to the electrons in the other orbit BC of the pair I have made by means of two distinct approximations. In the first of these I have assumed that this force equals what it would be, if half the electrons in the orbit BC were concentrated at B, the nearest point in it to A, and half at C, the furthest point from A. This gives only a rough estimate of the terms in the equation representing the ratio ν/ν_0 due to the electrons in the various orbits outside of the inner one. As, however, all these terms add up to only 15 or 20 per cent of the value of the term due to the innermost orbit (expression 6), the error thereby introduced does not appear to be enormous. In the second approximate computation of the force acting on the electron at A, due to the electrons in the orbit BC, I have assumed the electricity of the electrons in BC to be uniformly distributed along the orbit. The results of these computations will be given in a subsequent note. They do not differ much from those obtained from the first approximate computation.

If we calculate the radii of the orbits, we find that, in general, the distances between the electrons in a pair of orbits and the electrons in another pair of orbits are greater in comparison with those radii than as represented in the figure. Hence the influence of electrons in outer orbits is small, and that of electrons in inner orbits approximates to what it would be, if they were at the nucleus.

To calculate the velocity of an electron, say at A, we first calculate the angle α in the figure as follows: Let N' be the total number of electron charges inside the orbits *A B C D*. N' then equals the atomic number of the chemical element N less the number of electrons inside the orbits *A B C D*. Assuming that half the charge in the orbit *BC* is concentrated at *B* and the other half at *C*, equating to zero the horizontal components of the forces due to the nuclear charge and to the electrons in and inside of the orbits *A B C D* and reducing we get the equation

$$cos^3\alpha = \frac{1}{\frac{8}{n}N' - 1}, \tag{7}$$

which gives us the value of the angle α.

Equating the radial components of the forces acting on an electron at A to the centripetal acceleration, multiplying by a^2, and substituting the value of N' from equation 7, we get the equation

$$mv^2a = e^2\left(\frac{n}{8}tan^3\alpha - s_n\right) \tag{8}$$

where

$$s_n = {}^1/_4 \sum_{s=1}^{s=n-1} cosec\, \frac{s}{n} \tag{9}$$

The velocities of the electrons other than the two in the inner orbit are small as compared with the velocity of light, and the correction for the change of the mass of an electron with its velocity is, therefore, negligible. Neglecting this change and combining equation 8 with the angular momentum law (equation 2) we get for the kinetic energy of the electron

$${}^1/_2\, mv^2 = \frac{2\pi^2e^4m}{h^2\tau^2}\left(\frac{n}{8}\,tan^3\alpha - s_n\right)^2 \tag{10}$$

where the angle α is given by equation 7, and s_n, by equation 9.

In systems of the kind considered, the potential energy of the electrons equals twice their kinetic energy with the negative sign before it.[3] Hence, the total energy, kinetic plus potential, is minus the kinetic energy. Substituting the expression for the total energy of all the electrons with one electron removed from the inner orbit, and with this electron in place in equation 3, and dividing by $h\nu_o$, we get

$$\frac{\nu}{\nu_o} = 2(-N.25)^2\left(1+{}^1/_4\,\beta^2+{}^1/_8\,\beta^4+\ldots\right) - N^2\left(1+{}^1/_4\beta'^2+{}^1/_8\,\beta'^4+..\right)$$
$$+ \Sigma\, \frac{2n}{\tau^2}\left(\frac{n}{8}\,tan^3\alpha - s_n\right)^2 - {}_n\Sigma\, \frac{2n}{\tau^2}\left(\frac{n}{8}tan^3\alpha' - s_n\right)^2 \tag{11}$$

as the expression for the critical absorption frequency of the chemical element divided by the Rydberg constant.

Table 1 contains the calculated and the observed values of the ratio ν/ν_0. The observed values I have taken from table 2 of the report on Data Relating to X-Ray Spectra which I compiled for the National Research Council. Column 4 in the table contains the observed values, and column 3 the values calculated according to the following scheme:

$$n_1 = 2, \quad n_2 = 4, \quad n_3 = 4, \quad n_4 = 9, \quad n_5 = 9, \quad n_6 = 16,$$
$$\tau_1 = 1, \quad \tau_2 = 2, \quad \tau_3 = 2, \quad \tau_4 = 3, \quad \tau_5 = 3, \quad \tau_6 = 4.$$

TABLE 1

K CRITICAL ABSORPTION FREQUENCIES

CHEMICAL ELEMENT	ATOMIC NUMBER	FREQUENCIES DIVIDED BY RYDBERG CONSTANT ν/ν_0		
		Calculated	Observed	Calculated
Magnesium	12	103.2	95.8	92.5
Sulphur	16	187.4	181.8	173.3
Calcium	20	297.7	297.5	279.7
Iron	26	521.0	523.8	494.9
Selenium	34	923.3	930.8	888.7
Molybdenum	42	1454.0	1474.0	1411.0
Tin	50	2125.0	2148.0	2063.0
Cerium	58	2918.0	2970.0	2860.0
Dysprosium	66	3896.0	3948.0	3820.0
Tungsten	74	5043.0	5118.0	4954.0
Lead	82	6404.0	6463.0	6270.0
Uranium	92	8468.0	8477.0	8345.0

It appears that, except in the case of the elements magnesium and sulphur, the calculated values in column three do not differ from the observed values by as much as two per cent. Considering the fact that the equations contain no undetermined constants after the distribution law has been fixed and considering the fact that various influences have been neglected, such as magnetic forces, forces due to electrons in outer orbits, the possible influence of electrons which may be forming bonds with other atoms, etc., the close agreement between the calculated and observed values appears extraordinary.

I have also calculated the absorption frequencies, assuming a distribution according to the scheme

$$n_1 = 2, \quad n_2 = 8, \quad n_3 = 18, \quad n_4 = 32,$$
$$\tau_1 = 1, \quad \tau_2 = 2, \quad \tau_3 = 3, \quad \tau_4 = 4.$$

The calculated values based on this scheme do not differ very much from those contained in column 3 of the table. It appears, therefore, that the calculation of the *K* critical absorption frequencies does not furnish a very sensitive method of determining exactly what the distribution of electrons is. It is important to note, however, that two electrons have a quantum number of one, sixteen electrons have a quantum number of two, thirty-six electrons have a quantum number of three, etc.

On examining the data closely we find a systematic deviation of the calculated from the observed values. This deviation becomes most marked in the elements of low atomic number. It lies in the same direction as the well-known difference between the observed and calculated ionizing potentials of helium.

In order to see whether a better representation of facts can be obtained by supposing that the two inner electrons revolve in opposite directions in separate orbits, I have made the calculations on that basis. The only difference in formula 11 occurs in the terms representing the innermost orbit. The first two terms of equation 11 must be replaced by the single term.

$$(N-1)^2 (1 + {}^1/_4 \beta'^2 + {}^1/_8 \beta'^4 + \ldots) \qquad (12)$$

Column 5 of the table contains the results of the computations. It appears from the data of column 5 that the observed and calculated values differ from each other by amounts up to $4^1/_2\%$. A systematic variation exists which increases as the atomic weight decreases, and which lies in the opposite direction to that represented by the data of column 3.

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[1] *Science*, May 21, 1920.

[2] Fall Meeting of the National Academy of Sciences, 1920; *Physic. Rev.*, March, 1921, p. 431.

[3] This can be proved easily for the particular case in question. For a proof of the theorem in a more general form see A. Sommerfeld, *Atombau und Spektrallinien*, Appendix 5.

ON THE CALCULATION OF THE X-RAY ABSORPTION FREQUENCIES OF THE CHEMICAL ELEMENTS (SECOND NOTE)

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Communicated July 25, 1921

In a note presented to the National Academy of Sciences[1] I have given some computations of the K critical absorption frequencies of the chemical elements based on the Rutherford-Bohr theory of the structure of atoms and the mechanism of radiation. In these computations I have assumed that the electrons were distributed in circular orbits, which did not lie in planes passing through the nucleus of the atom.

In order to estimate roughly the forces exerted on an electron in one orbit (A in the figure of the previous note) due to the electrons in the parallel orbit, I assumed that they were the same as if the charges of the electrons in the orbit BC were concentrated, half at the nearest point